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铋(Ⅲ)四氢吡咯氨荒酸配合物[Bi(S$_2$CNC$_4$H$_8$)$_3$]$_2$的合成和晶体结构

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关键词: 双核铋(Ⅲ)配合物 四氢吡咯氨荒酸 晶体结构
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The Bismuth (Ⅲ) Complex with Dithiotetrahydropyrrolocarbamate: Synthesis and Crystal Structure of [Bi(S$_2$CNC$_4$H$_8$)$_3$]$_2$

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The novel bismuth (Ⅲ) complex with dithiotetrahydropyrrolocarbamate, [Bi(S$_2$CNC$_4$H$_8$)$_3$]$_2$ has been synthesized. The crystal structure has been determined by X-ray single crystal diffraction. The crystal belongs to monoclinic with space group $C2/c$, a = 1.6356(9) nm, b = 1.1875(6) nm, c = 2.3954(13) nm, β = 100.741(8)°, Z = 4, V = 4.571(4) nm^3, D_x = 1.882g · cm^{-3}, μ = 8.267mm^{-1}, $F(000)$ = 2512, R = 0.0404, wR = 0.0622. In this binuclear complex, each Bi (Ⅲ) is seven coordinate with a distorted pentagonal bipyramidal geometry. CCDC: 179924.

Keywords: binuclear bismuth (Ⅲ) complex dithiotetrahydropyrrolocarbamate crystal structure

0 Introduction

The chemistry of organotin (Ⅳ) dithiocarbamate complexes were extensively studied due to their biological activities[1-5]. To date, a large number of transition-metal complexes with dithiocarbamate have been synthesized and structurally characterized[6-9], including Ni(S$_2$CNC$_4$H$_8$O)$_2$, Cu(S$_2$CNC$_4$H$_8$)$_2$, Zn(S$_2$CNC$_4$H$_8$)$_2$ and Fe(S$_2$CNC$_4$H$_8$O)$_2$(DMF) . However, the chemistry of main-group metal complexes with dithiocarbamate has been scarcely studied, and a few reports have appeared on the syntheses and structures of the bismuth (Ⅲ) complexes with dithiocarbamate. Herein, we report the synthesis and structure of a novel binuclear bismuth (Ⅲ) complex [Bi(S$_2$CNC$_4$H$_8$)$_3$]$_2$.

1 Experimental

1.1 Synthesis of Bismuth (Ⅲ) Complex with Dithiotetrahydropyrrolocarbamate

Sodium dithiotetrahydropyrrolocarbamate was prepared by the method described in literature[10] . The elemental analyses were performed on a PE-2400-II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer, as KBr discs.

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To an aqueous solution of $Bi(NO_3)_3 \cdot 5H_2O$ (0.1 mmol) and mannite (1.0mmol) was added an aqueous solution of sodium dithiotetrahydropyrrolocarbamate (3.0mmol) and stirred for 0.5h at 30℃. The yellow solids were obtained by filtration. The product was recrystallized in acetonitrile to give yellow crystals 0.55g, yield 85%, m.p. 323℃ (dec); IR (KBr) ν (cm^{-1}): 2967, 2867, 1496, 1437, 1385, 1149, 1028, 939, 914, 447; Anal. Calcd(%) for $C_{30}H_{48}N_6S_{12}Bi_2$ (M_r = 1295.42): C, 27.82; H, 3.73; N, 6.49; S, 29.70. Found(%): C, 27.74; H, 3.57; N, 6.52; S, 29.54.

1.2 Crystal Structure Determination and Refinement

An yellow crystal having approximate dimensions of 0.20 × 0.20 × 0.15mm^3 was selected for the experiment and sealed in a glass capillary. X-ray diffraction were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.071073nm) at 299(2) K using the ω-2θ scan technique. A total of 11317 reflections were collected in the range of 1.73° < θ < 25.03° and 3838 reflections were independent (R_{int} = 0.0703), of which 1973 reflections were observed ($I > 2\sigma(I)$). The crystal belongs to monoclinic with space group $C2/c$, a = 1.6356(9) nm, b = 1.1875(6) nm, c = 2.3954(13) nm, β = 100.741(8)°, Z = 4, V = 4.571(4) nm^3, D_x = 1.882g · cm^{-3}, μ = 8.267mm^{-1}, $F(000)$ = 2512. The structure was solved by direct method and difference Fourier syntheses using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The weighting scheme was $w = 1/[S^2(F_o^2) + (0.0169P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement was converged to the final R = 0.0394, wR = 0.0562 ($I \geqslant 2\sigma(I)$), $(\Delta/\sigma)_{max}$ = 0.001 and S = 0.821. The largest difference peak and hole were 958e · nm^{-3} and −767e · nm^{-3}, respectively.

CCDC: 179924.

2 Results and Discussion

2.1 IR Spectra of Bismuth (Ⅲ) Complex with Dithiotetrahydropyrrolocarbamate

The assignment of IR bands of this binuclear complex has been made by comparison it with the IR spectra of complex with sodium dithiotetrahydropyrrolocarbamate. A new absorption band appears at 447cm^{-1} which is the characteristic vibrations of Bi-S bond formed.

One obvious feature of the IR spectra is the similarity of the stretching bands arising from the dithiotetrahydropyrrolocarbamate ligand. The relatively high value (1496cm^{-1}) for ν(C-N) is similar to that reported for analogous tin complexes[11-13]. It is suggested that the dithiotetrahydropyrrolocarbamate ligand of this complex is linked to Bi atom in a bidentate fashion.

In IR spectra, the important bands arise from $\nu(CS_2)_{asym}$ and $\nu(CS_2)_{sym}$ appear at 1149 cm^{-1} and 1028cm^{-1}, respectively. The $\Delta\nu$ value [$\nu(CS_2)_{asym} - \nu(CS_2)_{sym}$] is 121$cm^{-1}$, which is much smaller than the $\Delta\nu^*$ for the R_2NCS_2R' [14], but is larger than the $\Delta\nu'$ for the corresponding sodium dithiotetrahydropyrrolocarbamate. This shows that the dithiotetrahydropyrrolocarbamate ligand is coordinated to Bi atom in an anisobidentate fashion[10].

2.2 Molecular Structure of Bismuth (Ⅲ) Complex with Dithiotetrahydropyrrolocarbamate

The molecular structure and molecular packing in the unit cell are shown in Fig. 1 and 2, respectively. The selected bond lengths and angles is listed in Table 1.

In this binuclear complex, each Bi atoms is seven coordinate with a distorted pentagonal bipyramidal geometry. Each of central Bi atoms is surrounded equatorially by five S atoms and axially by two S atoms. Two of the six bidentate ligands are bridged in such a way that each sulfur atom is simultaneously bonded to both Bi atoms. In complex, the bismuth center is bonded to three $S_2CNC_4H_8$ groups with Bi-S distances 0.2781(3) nm, 0.2848(3) nm, 0.2871(3) nm, 0.2599(3) nm,

Table 1　Selected Bond Distances(nm) and Angles(°) of Complex

Bi(1)-S(4)	0.2597(3)	Bi(1)-S(1)	0.2780(3)	Bi(1)-S(5)	0.2813(3)
Bi(1)-S(2)	0.2846(3)	Bi(1)-S(3)	0.2873(3)	Bi(1)-S(6)	0.2979(3)
Bi(1)-S(6A)	0.3404(4)	N(1)-C(1)	0.131(9)	N(1)-C(2)	0.146(9)
N(1)-C(5)	0.145(3)	N(2)-C(6)	0.130(9)	N(2)-C(7)	0.145(6)
N(2)-C(10)	0.147(5)	N(3)-C(11)	0.131(8)	N(3)-C(12)	0.148(8)
N(3)-C(15)	0.147(8)	S(1)-C(1)	0.1721(9)	S(2)-C(1)	0.1707(9)
S(3)-C(6)	0.1696(9)	S(4)-C(6)	0.1730(9)	S(5)-C(11)	0.1723(8)
S(6)-C(11)	0.1695(9)	C(2)-C(3)	0.149(2)	C(3)-C(4)	0.149(6)
S(4)-Bi(1)-S(1)	85.8(2)	S(4)-Bi(1)-S(5)	91.7(5)	S(1)-Bi(1)-S(5)	73.3(1)
S(4)-Bi(1)-S(2)	86.6(5)	S(1)-Bi(1)-S(2)	63.8(7)	S(5)-Bi(1)-S(2)	137.1(5)
S(4)-Bi(1)-S(3)	65.3(9)	S(1)-Bi(1)-S(3)	137.1(5)	S(5)-Bi(1)-S(3)	134.7(5)
S(2)-Bi(1)-S(3)	82.5(5)	S(4)-Bi(1)-S(6)	93.5(2)	S(5)-Bi(1)-S(6)	61.5(1)
S(2)-Bi(1)-S(6)	161.3(4)	S(3)-Bi(1)-S(6)	80.5(9)	S(6A)-Bi(1)-S(6)	78.1(5)
S(6A)-Bi(1)-S(5)	79.4(6)	S(6A)-Bi(1)-S(2)	89.2(5)	S(6A)-Bi(1)-S(1)	129.1(2)
S(6A)-Bi(1)-S(3)	72.1(7)	S(6A)-Bi(1)-S(4)	137.3(5)	C(1)-S(1)-Bi(1)	88.7(3)
C(1)-S(2)-Bi(1)	86.8(3)	C(6)-S(3)-Bi(1)	83.2(3)	C(6)-S(4)-Bi(1)	91.6(3)
C(11)-S(5)-Bi(1)	91.7(3)	S(2)-C(1)-S(1)	120.5(6)	S(6)-C(11)-S(5)	120.2(6)
N(1)-C(1)-S(2)	120.6(7)	N(2)-C(6)-S(3)	122.7(7)	N(3)-C(11)-S(5)	118.6(7)
C(11)-S(6)-Bi(1)	86.7(3)	S(3)-C(6)-S(4)	119.8(6)	N(1)-C(1)-S(1)	118.9(7)
N(2)-C(6)-S(4)	117.5(7)	N(3)-C(11)-S(6)	121.2(7)		

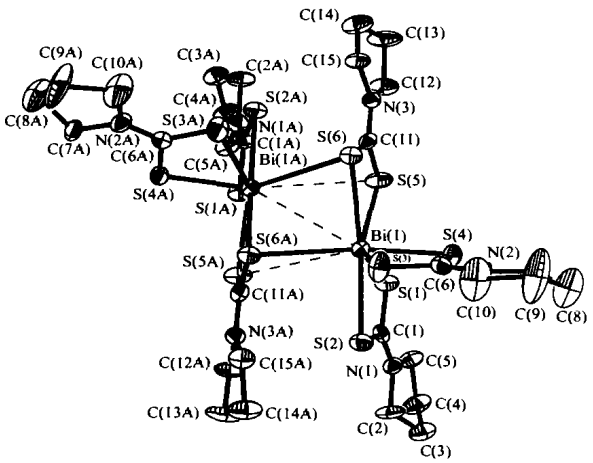

Fig. 1　Molecular structure of binuclear complex

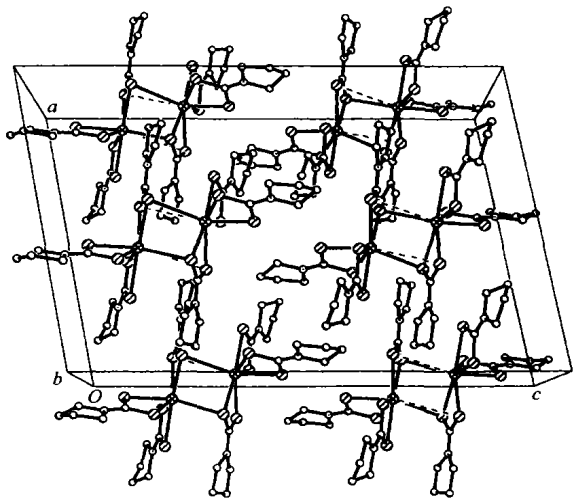

Fig. 2　Projection of the unit cell of binuclear complex

0.2814(3)nm, and 0.2979(3)nm. It is evident that a longer Bi-S intermolecular interaction is also present resulting in a centrosymmetric bridged binuclear complex. With the Bi(1)-S(6A) interaction included, the overall coondination geometry around the bismuth center is a seven coordinate pentagonal bipyramid.

Inspection of bond lengths clearly shows that non-bridging S atoms form coordination bonds that are at least 0.0425nm shorter than those of the bridging atoms. All Bi-S bond distances are generally longer than the sum of the corresponding covalent or atomic radii. In addition, one of the two Bi-S bonds of each ligand is always significantly shorter than the other.

In this complex, three $S_2CNC_4H_8$ ligands bond to Bi atom in bidentate fashion. The bond angles, forming by sulfur atoms of $S_2CNC_4H_8$ ligand occupying equatorial place, deviate from the central angle of standard pentagon, and the sum of these angles is 375.9°, which shows that these atoms are not co-planar. Furthermore, due to the constraint of the chelate, the an-

gles S(1)- Bi(1) -S(2) and S(5) -Bi(1) -S(6) are not 90° but only 63.8(9)° and 61.5(2), the S(2) and S(6) atoms can not exactly occupy the corresponding trans axial position of the pentagonal bipyramid, the angle S(2) -Bi(1) -S(6) being axial place is 161.3(7)°, which deviates from linear angle 180°. These data indicate that each Bi atom has a distorted pentagonal bipyramidal coordination geometry.

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